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18 September 2003 (18.09.2003) IT
- (71) Applicants (for all designated States except US): ENI S.p.A. [IT/IT]; Piazzale E. Mattei, 1, I-00144 Rome (IT). INSTITUT FRANCAIS DU PETROLE [FR/FR]; 1 et 4, Avenue du Bois Préau, Rueil Malmaison (FR). ENITECNOLOGIE S.p.A. [IT/IT]; Via F. Maritano 26, I-20097 San Donato (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): MARETTO, Cristina [IT/IT]; Via Padre Granata 11, I-26900 Lodi (IT). PEDERZANI, Giovanni [IT/IT]; Via E. Fermi 12/B, I-20097 San Donato (IT).
- (74) Agents: DE GREGORI, Antonella et al.; Ing. Barzanó & Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).
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(54) Title: PROCESS FOR THE CHARGING OF A CATALYST INTO A REACTOR SUITABLE FOR REACTIONS IN HETEROGENEOUS PHASE

(57) Abstract: Process for the charging of a catalyst and for the running of a reactor in which reactions take place in multiphase systems, wherein a gaseous phase prevalently consisting of CO and H₂ is bubbled into a suspension of a solid in the form of particles (catalyst) in a liquid (prevalently reaction product), according to the Fischer-Tropsch technology.

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PROCESS FOR THE CHARGING OF A CATALYST INTO A REACTOR SUIT-
ABLE FOR REACTIONS IN HETEROGENEOUS PHASE

The present invention relates to a process for charging
10 ing a catalyst into a reactor suitable for reactions in
heterogeneous phase.

More specifically, the present invention relates to a
process for charging a catalyst into a reactor suitable for
reactions in heterogeneous phase and for its running, com-
15 bined with reactions which take place in fluidized multi-
phase systems.

Even more specifically, the present invention relates
to a process for the charging of a catalyst and for the
running of a reactor in which reactions take place in mul-
20 tiphase systems, wherein a gaseous phase, prevalently con-
sisting of CO and H₂, is bubbled into a suspension of a
solid in the form of particles (catalyst) in a liquid
(prevalently reaction product), according to the Fischer-
Tropsch technology.

25 The Fischer-Tropsch technology is known in literature,

for preparing hydrocarbons from mixtures of gas based on hydrogen and carbon monoxide, conventionally known as synthesis gas. A document which summarizes the main works on the Fischer-Tropsch synthesis reaction is represented by
5 Sie and Krishna, Appl. Catalysis A: General (1999), 186, 55-70.

The Fischer-Tropsch technology is generally based on the use of slurry reactors, reactors which are normally used in relation to chemical reactions which are carried
10 out in multiphase systems in which a gaseous phase is bubbled into a suspension of a solid in a liquid. In the case of Fischer-Tropsch, the gaseous phase consists of synthesis gas, with a molar ratio H_2/CO ranging from 1 to 3, the liquid phase, at the reaction temperature, prevalently consists of the reaction product, i.e. essentially linear hydrocarbons with a high number of carbon atoms, and the
15 solid phase is prevalently represented by the catalyst.

The Fischer-Tropsch reaction is a exothermic reaction which, for its industrial embodiment, requires internal
20 heat exchanger devices, for removing the heat produced and for controlling the thermal profile inside the reactor.

The objective of the present invention is the running of the phases which are not included in the normal operating conditions for Fischer-Tropsch reactions and which are
25 particularly critical for the catalyst performances, such

as for example:

- charging;
- start-up/conditioning;
- make-up (subsequent additions of catalyst);
- 5 - temporary or definite shut-down of the reaction section;
- re-start-up after the temporary shut-down.

In scientific literature, for example published in Australian patent application AU 200066518 A1, a process is
10 described for treating, in the charging phase, a catalyst for Fischer-Tropsch reactions which are carried in fluidized multiphase reactors and for running these during the shut-down or re-start-up phases.

The Applicants have now found an alternative process
15 to that of the known art, for charging a catalyst into a bubble column slurry reactor and methods for the running of said reactor outside the normal operating conditions. The description of these methods is effected with the help of figure 1 enclosed.

20 An object of the present invention therefore relates to a process for the charging of a catalyst into a bubble column slurry reactor (B) in start-up phase which comprises:

- a) incorporating the catalyst, previously reduced, in a
25 matrix of paraffinic waxes, for example in the form of

pellets, tablets or granules, solid at room temperature;

- b) melting and collecting the paraffinic matrix (1) in a vessel (A), maintained at a high temperature, together with a diluent (2) which is miscible with the molten paraffinic matrix and which is in liquid form both under the conditions present in the container and at room temperature, a stream of inert gas (3) being distributed in said vessel (A) from the bottom so as to obtain a sufficiently homogeneous suspension;
- c) pressurizing the vessel (A), in which the complete melting of the paraffinic matrix has been effected, at a pressure higher than that of the reactor (B) maintaining the system fluidized by the continuous introduction of inert gas from the bottom of said vessel;
- d) transferring, due to the pressure change, the diluted solution (4) from the vessel (A) under pressure to the reactor (B), initially empty, maintained at a temperature higher than or equal to that present in the vessel (A) flushed in turn from the bottom with inert gas (5);
- e) repeating steps (b) to (d) until a suspension level is reached in the reactor (B) which is sufficient for

aligning the optional external equipment (E) envisaged for the treatment of the suspension (for example, degasifier, liquid-solid separators, pumps, etc.);

5 f) repeating steps (b) to (d) until the normal operating suspension level is reached in the reactor (B) and in the optional external equipment (E) envisaged for the treatment of the suspension;

g) feeding the synthesis gas (6) diluted with an inert
10 gas to the base of the reactor (B).

According to the present invention, the inert gas can consist, for example, of nitrogen or, preferably, purified natural gas.

The catalyst is englobed in paraffinic waxes in the
15 form of cylindrical blocks, wherein the quantity of wax ranges from 30 to 70% by weight. Any catalyst capable of being active in Fischer-Tropsch reactions can be used in the process object of the present invention. The preferred catalyst, according to the present invention, is based on
20 Co dispersed on a solid carrier consisting of at least one oxide selected from one or more of the following elements: Si, Ti, Al, Zr, Mg. Preferred carriers are silica, alumina or titania and their mixtures.

The cobalt is present in the catalyst in quantities
25 ranging from 1 to 50% by weight, generally from 5 to 35%

with respect to the total weight.

The catalyst used in the process, object of the present invention, can comprise further additional elements. It can comprise, for example, with respect to the total, from
5 0.05 to 5% by weight, preferably from 0.1 to 3%, of ruthenium and from 0.05 to 5% by weight, preferably from 0.1 to 3%, of at least a third element selected from those belonging to group 3 (IUPAC regulation). Catalysts of this type are known in literature and described, together with their
10 preparation, in European patent 756,895.

Further examples of catalysts are again based on cobalt but containing, as promoter element, tantalum in quantities of 0.05-5% by weight, with respect to the total, preferably 0.1-3%. These catalysts are prepared by first
15 depositing a cobalt salt on the inert carrier (silica or alumina), for example by means of the dry impregnation technique, followed by a calcination step and, optionally, a reduction and passivation step of the calcined product.

A derivative of tantalum (particularly tantalum alcoholates) is deposited on the catalytic precursor thus obtained, preferably with the wet impregnation technique followed by calcination and, optionally, reduction and passivation.
20

The catalyst, whatever its chemical composition may
25 be, is used in the form of a finely subdivided powder hav-

ing an average diameter of the granules ranging from 10 to 250 μm .

The catalyst, englobed in the paraffinic matrix, is brought to a temperature higher than or equal to 150°C, for example, from 150 to 220°C, and diluted with a diluent liquid at those temperatures, and also at room temperature, for example with an oligomer of $\text{C}_6\text{-C}_{10}$ α -olefins, until a concentration of solid ranging from 10 to 50% by weight is obtained. After the complete melting of the paraffinic matrix, the suspension is transferred into the reactor (B), maintained at a temperature higher than or greater than that of the melting vessel (A), by means of an internal heat exchanger. Under normal operating conditions, the exchanger serves for removing the reaction heat produced and maintaining the conditions more or less isothermal in the whole reaction volume.

During the transfer of the suspension, the reactor (B) is at a pressure lower than that present in the charging vessel (A) in order to favour the passage of the suspension from the vessel to the reactor due to the difference in pressure. The pressure in the charging vessel (A) is generally higher than that present in the reactor (B) by about 0.2-0.4 MPa whereas the pressure inside the reactor is maintained at about 0.1-1 MPa. For the whole duration of the transfer process, a stream of inert gas (5) is main-

tained at the bottom of the reactor (B) to guarantee the suspension of the catalyst, thus preventing its sedimentation.

Both the temperature and pressure present inside the reactor (B) during the charging phase are lower than the values present during regime synthesis conditions. The Fischer-Tropsch reaction is in fact carried out at temperatures equal to or higher than 150°C, for example ranging from 200 to 350°C, maintaining a pressure ranging from 0.5 to 5 MPa inside the reactor. More significant details on Fischer-Tropsch reactions are available in "Catalysis Science and Technology", vol. 1, Springer-Verlag, New York, 1981.

In order to reach the normal operating level inside the reactor (B) and all the optional apparatuses (E) envisaged for the treatment of the suspension, the melting, dilution and transfer from the charging vessel (A) to the reactor (B) are repeated various times. In relation to the concentration of the catalyst desired and plant production capacity, this operation can be repeated, for example, from 2 to 30 times.

During the first and subsequent charging steps, the reactor (B) is kept isolated from the optional equipment (E) envisaged for the treatment of the suspension, until an adequate suspension level is reached in the reactor itself

enabling it to be aligned with said equipment (E). The charging steps are then completed until the normal operating level is reached. The vessels (A) and (B) have outlets (13) for the recovery of the vapour phase (inert gas and/or non-reacted synthesis gas, and/or synthesis reaction products in vapour phase under the reaction conditions).

At the end of the charging phase, before bringing the system to the normal reaction and production conditions (14), a conditioning phase of the catalyst is activated. More specifically, at the end of the charging, the reactor (B) is in temperature conditions ranging from 150 to 220°C and a pressure ranging from 0.1 to 1 MPa, and is continuously fed with inert gas. The conditioning phase of the catalyst comprises:

- a) regulating the temperature and pressures at values suitable for the conditioning, i.e. within the range of 200-230°C and 0.5-1.5 MPa;
- b) gradually substituting the inert gas with synthesis gas, up to a concentration of inert gas ranging from 5 to 50% by volume and maintaining a partial water pressure (co-product of the Fischer-Tropsch synthesis reaction) lower than 1.0 MPa, preferably lower than 0.5 MPa, more preferably lower than 0.3 MPa;
- c) maintaining the conditions of point (b) for 24-72 hours;

- d) gradually increasing the pressure inside the reactor (B) up to regime values (0.5-5 MPa);
- e) gradually reducing the concentration of inert gas to zero until regime conditions; and subsequently
- 5 f) gradually increasing the reaction temperature until reaching regime values (200-350°C).

Synthesis gas essentially consists of CO and H₂, possibly mixed with CH₄, CO₂ and inert gases in general; it has a H₂/CO molar ratio ranging from 1 to 3 and preferably
10 derives from steam reforming and/or partial oxidation of natural gas or other hydrocarbons, on the basis of the reactions described, for example, in U.S. patent 5,645,613. Alternatively, the synthesis gas can derive from other productions techniques such as, for example, autothermal re-
15 forming, C.P.O. (Catalytic Partial Oxidation) or from the gasification of coal with water vapour at a high temperature as described in "Catalysis Science and Technology", vol. 1, Springer-Verlag, New York, 1981.

When the reactor (B) is under regime conditions, periodic make-up of the catalyst is envisaged for compensating
20 losses (in activity and material) during the overall production cycle, for example by flushings effected in the liquid-solid separation section.

In order to carry out the make-up of the catalyst, it
25 is not only necessary to effect the melting of the pellets

and their possible dilution with a solvent, but it is also preferable to proceed with the conditioning of the fresh catalyst before introducing it into the reaction environment. There is therefore a specific melting and conditioning section for this function which is essentially based on:

- a vessel (C), equipped with an inlet for inert gas (3'), where the pellets of catalyst, after the addition of a solvent (8), are charged (7) and melted, similar to that adopted for the initial charging, preferably having smaller dimensions, which is run under the same conditions as those of the main charging vessel (A);

a reaction vessel (D), equipped with inlets for inert gas (5') and synthesis gas (6'), where the suspension is transferred (9) after melting, in which the catalyst undergoes the same conditioning process envisaged for the fresh catalyst used during the initial charging; said vessel (D) is designed for reaching higher pressures than those of the reactor (B) during normal operating conditions; after completing the conditioning procedure, in fact, the suspension is transferred (10) from the reaction vessel (D) to the main reactor (B) as a result of the pressure change.

The vessels (C) and (D) have outlets (13') for recov-

ering the vapour phase (inert gas and/or non-reacted synthesis gas, and/or products of the synthesis reaction in vapour phase under the reaction conditions).

At the end of the conditioning phase of the catalyst
5 and once the synthesis reactor (B) has been brought to regime conditions, the running of the latter can comprise a further two steps: stoppage (or shut down), with consequent reactivation, and a temporary stoppage phase, better known as stand-by.

10 The shut-down of a reactor (B) in which reactions are effected which take place in multiphase systems, wherein a gaseous phase, prevalently consisting of CO and H₂, is bubbled into a suspension of a solid in the form of particles (catalyst) in a liquid (prevalently reaction product), requires the following operating phases:

- i. gradual stoppage of the feeding of synthesis gas (6) and its gradual substitution with inert gas (5);
- ii. possible reduction of the operating pressure and temperature inside the reactor (B) to values close to
20 those of the conditioning phase;
- iii. discharging (4) of the suspension contained in the reactor (B) and (11) in the units associated therewith (E) and its recovery in the vessel (A) heated and flushed with inert gas (3); the transfer is effected
25 by means of the difference in pressure, the vessel (A)

having been previously brought to a pressure at least 3 bars lower than the reactor (B).

According to the present invention, the inert gas can consist, for example, of nitrogen or, preferably, of purified natural gas.

According to this embodiment of the present invention, once the suspension has been discharged from the reactor (B) and from the equipment (E) envisaged for the treatment of the suspension, such as degassing vessels and/or decanters and/or filters and other apparatuses such as recirculation pumps, and once the actions required for the shutdown phase have been completed, the reactor can be reactivated following the method described above, for example, for the charging phase.

The vessel (A) is designed to have a capacity which is such as to contain the volume of suspension present in the reactor (B) and in the other units (E), associated with the treatment of the suspension, at the moment of shut-down.

Should it not be necessary to empty the reactor (B) in the shut-down phase, in the case for example of a temporary stand-by phase, the latter comprises:

1. gradual stoppage of the feeding of the synthesis gas (6) and gradual substitution with inert and/or reducing gas, for example hydrogen (5) to keep the solid phase sufficiently dispersed in the suspension, at

the same time minimizing any possible deactivation phenomena;

2. possible reduction in the operating temperature and pressure to values close to those of the conditioning phase.

In this phase, the reactor (B) can be kept in line with the treatment section of the suspension (E) which is completely recycled, (11) and (12), to the reactor without the extraction of products. Alternatively, the reactor can be disaligned from the units (E) after removing the suspension from the equipment (E) directly connected to the reactor (B). The latter is preferably designed to have a capacity which is such as to also contain the volume of suspension present in the units (E) at the moment of temporary stand-by.

CLAIMS

1. A process for the charging of a catalyst into a slurry bubble column reactor (B) in activation phase which comprises:
- 5 a) incorporating the catalyst, previously reduced in a matrix of paraffinic waxes, solid at room temperature;
- b) melting and collecting the paraffinic matrix (1) in a vessel (A), maintained at a high temperature, together with a diluent (2) which is miscible with the molten
10 paraffinic matrix and which is in liquid form both under the conditions present in the vessel and at room temperature, a stream of inert gas (3) being distributed in said vessel (A) from the bottom so as to obtain a sufficiently homogeneous suspension;
- 15 c) pressurizing the vessel (A) in which the complete melting of the paraffinic matrix has been effected at a pressure higher than that of the reactor (B) maintaining the system fluidized by the continuous introduction of inert gas from the bottom of said vessel;
- 20 d) transferring, due to the pressure change, the diluted solution (4) from the vessel (A) under pressure to the reactor (B), initially empty, maintained at a temperature higher than or equal to that present in the vessel (A) flushed in turn from the bottom with inert gas
25 (5);

- e) repeating steps (b) to (d) until a suspension level is reached in the reactor (B) which is sufficient for aligning the optional external equipment (E) envisaged for the treatment of the suspension;
- 5 f) repeating steps (b) to (d) until the normal operating suspension level is reached in the reactor (B) and in the optional external equipment (E) envisaged for the treatment of the suspension;
- g) feeding the synthesis gas (6) diluted with an inert
10 gas to the base of the reactor (B).
2. The process according to claim 1, wherein the catalyst is englobed in paraffinic waxes in the form of pellets wherein the quantity of wax ranges from 30 to 70% by weight.
- 15 3. The process according to claim 1 or 2, wherein the catalyst comprises Co dispersed on a solid carrier consisting of at least one oxide selected from one or more of the following elements: Si, Ti, Al, Zr, Mg and their mixtures.
4. The process according to claim 3, wherein the cobalt
20 is present in the catalyst in quantities ranging from 1 to 50% by weight with respect to the total weight.
5. The process according to any of the previous claims, wherein the catalyst is used in the form of a finely subdivided powder with an average diameter of the granules ranging
25 from 10 to 250 μm .

6. The process according to any of the previous claims, wherein the catalyst englobed in the paraffinic matrix is brought to a temperature which is greater than or equal to 150°C and diluted with a diluent liquid at those temperatures, and also at room temperature, until a concentration of solid ranging from 10 to 50% by weight, is obtained.
7. The process according to claim 6, wherein the diluent consists of an oligomer of C₆-C₁₀ α-olefins.
8. The process according to any of the previous claims, wherein the pressure in the charging vessel (A) is higher than that present in the reactor (B) by about 0.2-0.4 MPa whereas the pressure inside the reactor is maintained at about 0.1-1 MPa.
9. The process according to any of the previous claims, wherein in order to reach the normal operating level inside the reactor (B) and all the optional pieces of equipment (E) envisaged for the treatment of the suspension, the melting, dilution and transfer operation from the charging vessel (A) to the reactor (B) is effected from 2 to 30 times.
10. A process for the conditioning of a catalyst contained in a bubble column reactor (B) suitable for reactions in heterogeneous phase, which comprises:
- a) regulating the temperature and pressures at values suitable for the conditioning, i.e. within the range

of 200-230°C and 0.5-1.5 MPa;

- b) gradually substituting the inert gas with synthesis gas, up to a concentration of inert gas ranging from 5 to 50% by volume and maintaining a partial water pressure (co-product of the Fischer-Tropsch synthesis reaction) lower than 1.0 MPa, preferably lower than 0.5 MPa;
- c) maintaining the conditions of point (b) for 24-72 hours;
- 10 d) gradually increasing the pressure inside the reactor (B) up to regime values (0.5-5 MPa);
- e) gradually reducing the concentration of inert gas to zero until regime conditions; and
- f) gradually increasing the reaction temperature until
- 15 regime values (200-350°C) are reached.
11. The process according to claim 10, wherein the flow-rate of inert gas of point (b) is regulated to maintain a partial water pressure lower than 0.3 MPa.

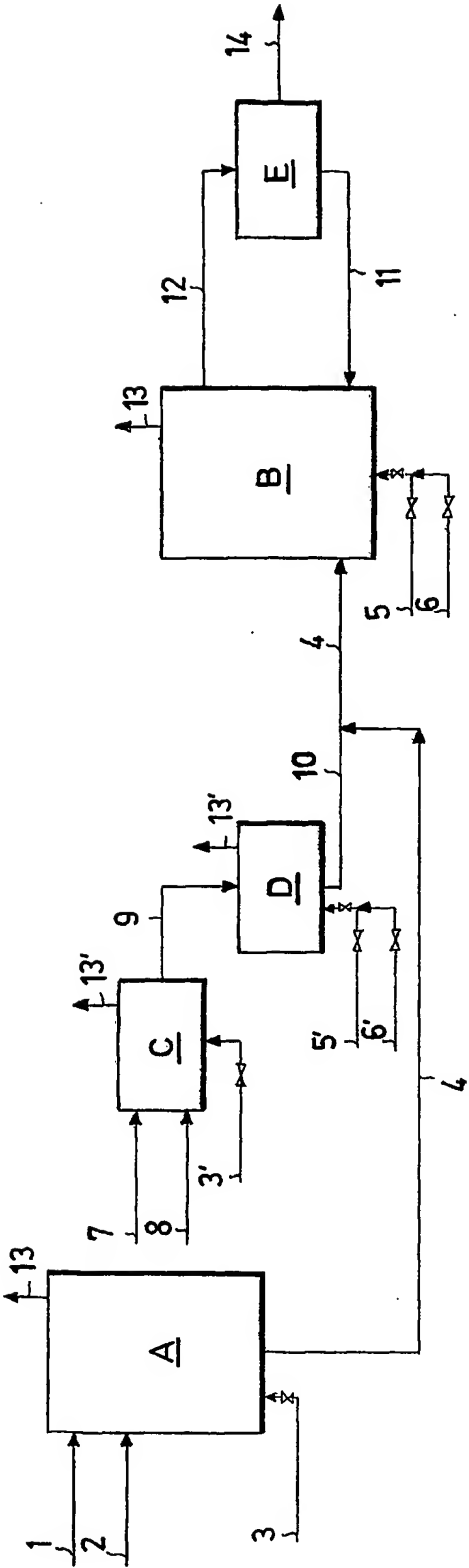


Fig.1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 2004/010650

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 03/068715 A (STEYNBERG ANDRE PETER ; SASOL TECH PTY LTD (ZA)) 21 August 2003 (2003-08-21) claims 1,2,6,8-13 page 7, line 16 - line 19 page 11, line 9 - line 14 page 13, line 25 - line 28	1-3,5,6, 8-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

& document member of the same patent family

Date of the actual completion of the international search

22 November 2004

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02/12/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Deurinck, P

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2004/010650

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this International Application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 21 0

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-9

a process for the charging of a catalyst into a slurry
bubble column reactor

2. claims: 10-11

a process for the conditioning of a catalyst contained in a
bubble column reactor

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/010650

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 03068715	A	21-08-2003	GB	2401112 A	03-11-2004
			WO	03068715 A1	21-08-2003